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PHOTODECOMPOSITION OF AQUEOUS SOLUTIONS OF DIAZONIUM SALTS IN THE PRESENCE OF MERCUROUS IONS.

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J. G. BOS, R. J. H. ALINK and C. J. DIPPEL
(Philips Research Laboratories N.V. Philips Gloeilampenfabrieken, Eindhoven - Netherlands).

Photodecomposition of aqueous solutions of o-hydroxydiazonium salts leads to *disproportionation* of mercurous ions, in contrast to p-aminobenzenediazonium salts where mercury results from *reduction* of mercurous ions by the photodecomposition products.

A photochemical process based on aromatic diazonium compounds and mercurous nitrate has been described [1]), out of which originated the metal-diazonium system for photographic reproduction [2]).

At the irradiated parts, mercury is formed as a result of the reaction between mercurous nitrate and the photodecomposition products of the diazonium compounds.

For this reaction water is necessary, which may be applied in the form of vapour or liquid.

Reduction of mercurous ions was originally supposed to be a general feature of the photodecomposition products of diazonium compounds. Later, we discovered that disproportionation of mercurous ions was an essential element of the reactions of the metal-diazonium process.

The nature of the photodecomposition product is of essential importance, both for the manner in which and the rate at which reactions with mercurous ions proceed.

Without further reference to the metal-diazonium process in question, the following experience is recorded as obtained with aqueous solutions of p-aminobenzenediazonium salts compared with those of o-hydroxydiazonium salts.

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[1]) U.S. 2.067.690 *R. J. H. Alink, K. H. Klaassens* and *H. J. Houtman* (to N.V. Philips Gloeilampenfabrieken), Chem. Abstr. **31,** 1315[2] (1937).

[2]) *R. J. H. Alink, C. J. Dippel* and *K. J. Keuning,* Philips Tech. Review **9,** 289 (1947/'48); C. J. *Dippel,* Phot. J. **90 B,** 34 (1950).

§ 1. The photodecomposition products.

1.1. *The photodecomposition products of p-aminobenzenediazonium salts.*

"Phenols" have long been accepted as being the products generally resulting from the action of light on diazonium compounds in the presence of water.

Proof of this has been given by *Schmidt* and *Maier* [3]) with acidified solutions, and by *de Jonge* and *Dijkstra* [4]) with diluted solutions, thus avoiding the appearance of coloured substances.

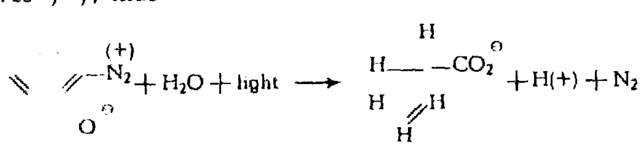
The point is that from the positively charged diazonium ion, under loss of nitrogen, a positively charged aryl ion arises, which binds a hydroxyl ion and forms a phenol, thus:

$$R{-}N_2^{(+)} + h\nu \rightarrow R^{(+)} + N_2$$
$$R^{(+)} + H_2O\ (\rightleftharpoons H^{(+)} + OH^{(-)}) \rightarrow R{-}OH + H^{(+)}$$

Consequently, p-aminophenols are formed from p-aminobenzenediazonium salts.

1.2. *The photodecomposition products of o-hydroxydiazonium salts.*

o-Hydroxydiazonium salts however react in an unexpected way. As a result of irradiation loss of nitrogen gives rise to an unstable molecule which transforms internally into cyclopentadiene derivatives [5]) [6]), thus:



Under special conditions also a phenolic substance is formed. Irradiation of a solution of o-hydroxybenzenediazonium acid sulphate in 50% H_2SO_4 gives catechol (yield 70%) and dimeric cyclopentadiene carboxylic acid (yield: 12%) [7]).

§ 2. Formation of metallic mercury from mercurous ions.

In aqueous solutions mercurous ions are in equilibrium with mercuric ions and metallic mercury according to:

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[3]) *J. Schmidt* and *W. Maier*, Ber. **64**, 767 (1931).
[4]) *J. de Jonge* and *R. Dijkstra*, Rec. trav. chim. **68**, 426 (1949).
[5]) *O. Süs*, Ann. **556**, 65, 85 (1944).
[6]) *J. de Jonge* and *R. Dijkstra*, Rec. trav. chim. **67**, 328 (1948).
[7]) *J. de Jonge*, *R. J. H. Alink* and *R. Dijkstra*, Rec. trav. chim. **69**, 1451 (1950).

$$Hg_2^{++} \rightleftarrows Hg^{++} + Hg$$

Ogg [8]) found a constant ratio between the concentrations of mercuric and mercurous ions in the presence of liquid metallic mercury, according to:

$$\frac{[Hg^{++}]}{[Hg_2^{++}]} \sim \frac{1}{120}$$

Mercury may be formed in two ways, 1) by reduction and 2) by disproportionation of mercurous ions. Thus, in photochemical reactions of diazonium compounds and mercurous ions where mercury is formed the question arises whether it is possible to discriminate between these two ways.

2.1. *Reduction of mercurous ions in irradiated aqueous solutions of p-aminobenzenediazonium salts.*

Substituted p-aminophenols are well-known developers in photography. The photodecomposition products of p-aminobenzenediazonium salts having the same structure are supposed to show also a reducing action on noble metal salts.

Through the gain of electrons (= reduction) mercurous ions transform into metallic mercury.

Reduction of mercurous ions is sufficient to cause the mercuric ions to disappear. The result according to:

$$Hg_2^{++} + 2\ominus \rightarrow 2\,Hg$$

shows complete transformation to metallic mercury, without any mercuric ions left.

In our experiments irradition of diluted solutions of p-aminobenzene diazonium salts and mercurous nitrate mostly results in nearly colourless solutions, in which at first no metallic mercury or only a small quantity is present. These colourless solutions show in course of time a deposition of metallic mercury together with a change into a brown colour.

The characteristics of the photodecomposition of the p-aminodiazonium compounds in the presence of mercurous ions may be formulated as:

a) quantitatively metallic mercury is formed in a *slow* reduction reaction of the mercurous ions by the photodecomposition product in the course of 10 to 18 hours *).

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[8]) *H. Remy,* Lehrbuch d. Anorg. Chemie II, 472 (Akad. Verlagsges., Becker und Erler, Kom. Ges. Leipzig, 1942).

*) With p-$(CH_3NH)C_6H_4N_2BF_4$ the reactions a, b and c already occur during irradiation.

b) the photodecomposition product itself is oxidized to a darkly coloured compound,

c) mercuric ions are not formed,

d) the presence of about N/10 HNO_3 in the solutions strongly retards the reduction reaction.

2.2. *Disproportionation of mercurous ions in irradiated aqueous solutions of o-hydroxydiazonium salts.*

Investigations with 1-hydroxy 2-diazonium 6-methyl benzene 5-sulfonic acid and mercurous nitrate — in molar ratios of 2 : 1 and 1 : 1 — in slightly acidified (HNO_3) diluted solutions showed contrary to § 2.1, that very soon after irradiation there is a quantitative transformation of the mercurous ions into metallic mercury and mercuric compound of the photodecomposition product in nearly equimolar quantities.

From analysis a net result has been computed according to:

$$1.00\ Hg_2^{++} \rightarrow 1.03\ (Hg^{++}) + 0.95\ Hg,$$

corresponding to disproportionation of mercurous ions.

Irradiation completely decomposes the said diazonium salt in the diluted solution into nitrogen and a photodecomposition product:

1.36 millimols of N_2 were generated from 1.34 millimols diazonium salt.

Some facts may be mentioned concerning a mercuric compound of the photodecomposition product which precipitated as a white jelly in the experiments. The mercuric compound is *insoluble* in diluted acids like HNO_3, H_2SO_4 and HCl. It is *soluble* in diluted alkalis like KOH and NH_4OH. These alkaline solutions remain clear on acidifying with HCl, but a mercuric compound is precipitated by diluted HNO_3 or H_2SO_4.

Irradiated solutions filtered from metallic mercury also remain clear on alkalising.

As in our case mercuric oxide is not precipitated in the alkaline solutions, a rather stable compound must have been formed by the binding of mercuric ions by the photodecomposition product. The mercuric compound(s) must have a low concentration of mercuric ions.

From the solubility product $1.38 \cdot 10^{-20}$ for $Hg(OH)_2$[9]) a concentration of mercuric ions $< 1.38 \cdot 10^{-24}$ g ion/l in a N/10 KOH solution is calculated. However from diluted ammoniacal solutions of the mercuric compound HgS is precipitated by H_2S. The solubility product of HgS is $4 \cdot 10^{-54}$ [10]).

[9]) *I. M. Kolthoff*, Chem. Weekblad **14**, 1020 (1917); Chem. Zentr. 1918, I, 163; *I. M. Kolthoff* and *V. A. Stenger*, "Volumetric Analysis" I, table III (Interscience Publishers, New York, 2nd Ed., 1942).

[10]) *A. I. Vogel*, Textbook of quant. inorganic Analysis, 13 (2nd Ed. Longmans, Green and Co., London—New York—Toronto, 1951).

The characteristics of the photodecomposition of o-hydroxy-diazonium salts in the presence of mercurous ions, in contrast to § 2.1, may be formulated as:

a) metallic mercury and mercury in the divalent state are generated in equivalent amounts,

b) metallic mercury is formed at a *relative fast* rate,

c) dyestuff is not formed in an appreciable amount,

d) the presence of N/10 HNO_3 in the irradiated solution does not hinder the formation of metallic mercury.

Apart from the fact that reduction of mercurous ions by 1-carboxyl 5-methyl cyclopentadiene 3-sulfonic acid as the photodecomposition product is not very probable, it is obvious from the characteristics that in the case of o-hydroxydiazonium salts the metallic mercury is not formed by reduction, but is due to disproportionation of mercurous ions.

From the equilibrium between mercurous and mercuric ions it is clear that metallic mercury is formed as soon as the equilibrium is displaced to the right by the binding of mercuric ions in the form of undissociated, insoluble or complex mercuric compounds.

$$Hg_2^{++} \rightarrow (Hg^{++}) + Hg.$$

The formation of mercury by binding of mercuric ions is a well known fact in inorganic chemistry, thus:

$$Hg_2^{++} + 2\,CN^- \rightarrow \text{undissociated } Hg(CN_2) + Hg.$$

$$Hg_2^{++} + S^{--} \rightarrow \text{insoluble } HgS + Hg$$

$$Hg_2J_2 + 2\,J^- \rightarrow \text{complex } (HgJ_4)^{--} + Hg.$$

Disproportionation by means of organic compounds is also known from literature.

Zappi [11]) found different organic compounds able to precipitate metallic mercury from an aqueous solution of mercurous nitrate. These compounds are acetylacetone and other enolic compounds, isonitriles and related compounds, ethylenic and acetylenic unsaturated compounds.

Zappi originally supposed mercurous nitrate to be reduced, but later on he discovered the formation of mercury to be due to the binding of mercuric ions by the organic compounds, which causes a displacement of the equilibrium to the right.

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[11]) *E. V. Zappi*, Bull. soc. chim. **51**, 54—59 (1932) (Chem. Abstr. **26**, 2706 (1932); *E. V. Zappi* and *A. F. Williams*, Bull. soc. chim. **51**, 1258—69 (1932) (Chem. Abstr. **27**, 904 (1933); *E. V. Zappi* and *Alice Manini*, Anales asoc. quim. argentina **26**, 89—105 (1938) (Chem. Abstr. **33**, 2063[3] (1939).

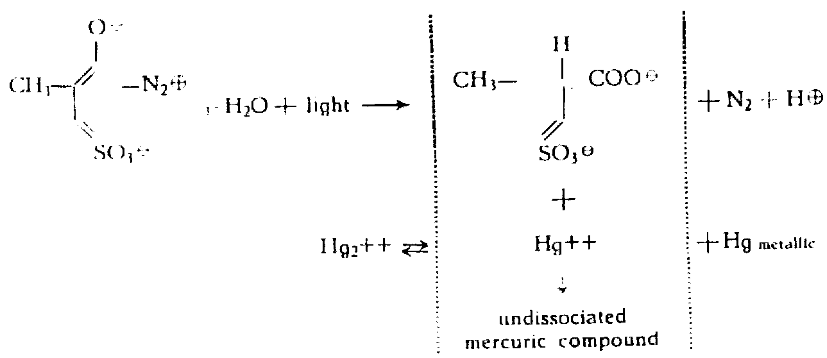
Kolthof and *Stenger* [12]) give a survey of the work done about the binding of mercuric salts or ions by unsaturated organic compounds. They refer to the work of *E. Biillmann* and *Agnes Hoff* (1916) and formulate from this the reaction of crotonic acid and mercuric salts as follows:

$$CH_3-CH=CH\cdot COOH + Hg^{++} + H_2O \rightarrow CH_3CH(OH)CH(Hg^{+})COOH + H^{+}.$$

This mercuric compound is soluble in alkali and from this solution HgS is precipitated by H_2S under liberation of β-hydroxy butyric acid.

The behaviour of unsaturated compounds towards mercuric ions supports our view that binding of mercuric ions by photodecomposition products such as cyclopentadiene compounds accounts for the formation of mercury from mercurous ions (*disproportionation*).

Thus we may formulate the principal reactions of the irradiation of diluted aqueous solutions of o-hydroxydiazonium salts in the presence of mercurous ions, as



Experimental part.

§ 3. Irradiation of aqueous solutions of diazonium salts in the presence of mercurous ions.

All parts have been mounted on an optical bench; the distances are in mm. By means of an enlarged picture on a separate screen the evolution of nitrogen bubbles and the origin of precipitates are observed (fig. 1).

The cell is filled with known quantities of diazonium and mercurous solutions. After mixing the solution is irradiated, while stirring with a small glass rod.

Preparation of a solution of mercurous nitrate.

In a closed bottle 30 g mercurous nitrate, 12 g mercury and 1 *l* water are mechanically shaken for 24 hours at 20° C to make a saturated solution. The filtered solution containing 13.525 g $Hg_2(NO_3)_2 \cdot 2\,H_2O$ per litre, to which some mercury is added, is stored in a brown bottle.

[12]) *I. M. Kolthoff* and *V. A. Stenger*, "Volumetric Analysis" I (1942), 222—224.

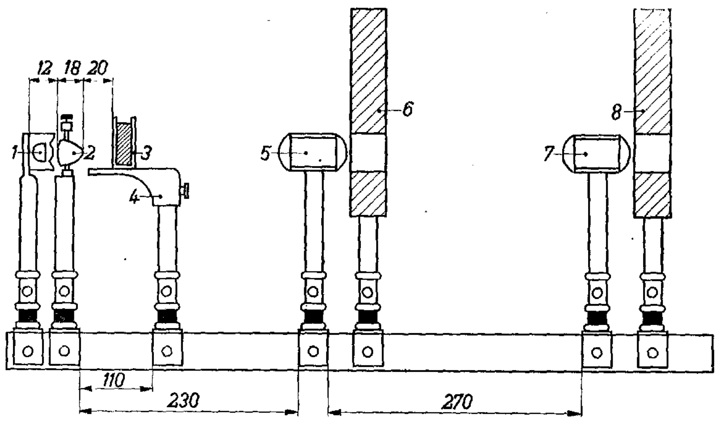


Fig. 1. Set-up of the apparatus.
1 = high intensity mercury vapour lamp SP 500.
2 = aspherical condenser (f = 12 mm, ∅ = 38 mm).
3 = glass cell.
4 = adjustable table.
5 = "Glaukar" anastigmate (f = 12 cm, F = 3.1).
6 and 8 = black screens with circular holes for 5 and 7.
7 = "Petzval" lens (f = 45 mm, 1 : 1 reproduction).

Preparation of the solutions of diazonium salts.

The diazonium salts are dissolved in distilled water and after shaking with some charcoal the solutions are filtered.

§ 4. Reduction of mercurous ions in irradiated aqueous solutions of p-aminobenzenediazonium salts.

The following table gives the results observed.

Dz—cpd No	Composite solution		mercury		colour	
	dz. cpd	$Hg_2(NO_3)_2 . 2H_2O$	during irrad.	after 18 hrs.	during irrad.	after 18 hrs.
I	0.44 % (0.017M)	0.75 % (0.0135M)	none	much	pink	dark brown
II	0.75 % 0.036M)	0.225 % (0.004M)	none	much	pink	dark brown
III	0.28 % (0.013M)	0.60 % (0.0105M)	much		dark brown	

I = p-(diethylamino) benzene diazonium borofluoride (M = 263)
II = p-(dimethylamino) benzene diazonium nitrate (M = 210)
III = p-(monomethylamino) benzene diazonium borofluoride (M = 221).
20 ml of I, II and III were irradiated respectively for 1, 1 and ½ min.

Analysis:

67.5 ml containing 0.297 g (1.13 millimols) of I and 0.506 g $Hg_2(NO_3)_2 . 2\,H_2O$ (corresponding to 1.80 millimols Hg) gave after irradiation 0.369 g or 1.84 millimols

Hg. The metallic mercury was analysed by collecting, washing, dissolving and potentiometric titration. (Mercuric and mercurous ions were absent in the irradiated solution).

Mercurous ions are quantitatively reduced by the photodecomposition product.

§ 5. Disproportionation of mercurous ions in irradiated aqueous solutions of o-hydroxydiazonium salts.

5.1 Qualitative experiments.

The following solutions of diazonium salts have been investigated:

IV 0.0019 M 1-hydroxybenzene 2-diazoniumborofluoride (M = 208)

V 0.023 M 1-hydroxy 2-diazoniumbenzene 5-sulfonic acid (M = 218)

VI 0.015 M 1-hydroxy 2-diazonium naphthalene 4-sulfonic acid ($+3\,H_2O$, M = 322).

VII 0.019 M 2-hydroxy 1-diazonium naphthalene 6-sulfonic acid (M = 268).

These solutions contained $Hg_2(NO_3)_2 . 2\,H_2O$ for 0.05 % (0.0009 M) in IV and 0.4 % (0.007 M) in V—VII. V—VII also contained 0.04 N HNO_3. IV was irradiated for ½ min, V—VII take 10—15 minutes.

In all cases metallic mercury is formed in such a way that the picture on the screen is darkened in 5 to 10 sec.

In IV also a nearly white flocky precipitate of the mercuric compound of the cyclopentadiene carboxylic acid is formed.

5.2 Quantitative investigations.

100—150 ml solution containing 1-hydroxy 2-diazonium 6-methylbenzene 4-sulfonic acid, mercurous nitrate and diluted HNO_3, the quantities of which are shown in the table at the end, were irradiated for 1 to 2 hours with a SP-500 mercury vapour lamp in a separate set-up and the generated nitrogen gas was collected by means of a slow current of CO_2 gas in an azotometer.

5.2.1 Nitrogen from the photodecomposition.

In duplicate measurements 1.34 millimols of 1-hydroxy 2-diazonium 6-methylbenzene 4-sulfonic acid gave

33.03 ml N_2 (756.7 mm Hg at 19° C) and

32.40 ml N_2 (759.2 mm Hg at 19° C),

corresponding to 1.37 and 1.35 millimols N_2.

Thus the diazonium salt at this concentration completely decomposes into nitrogen and the cyclopentadiene derivative, without an appreciable amount of an azo dyestuff being formed.

5.2.2 Quantitative determination of metallic mercury and mercury in the divalent state.

In a part of the irradiated solution the absence of mercurous ions was checked by KCl, no calomel being formed.

The whole solution, including mercury and a white precipitate, was ammoniacalised to 0.2 N NH_4OH in order to dissolve the white precipitate.

From this alkaline solution, containing the mercuric compound of the photodecomposition product, the metallic mercury was separated by centrifuging after addition of some ethanol. In the remaining solution divalent mercury was analysed by precipitating HgS and weighing.

The metallic mercury was dissolved in concentrated HNO_3 and after ammoniacalising precipitated as HgS and weighed.

As is shown in the table of the results, no mercuric ions nor mercury are formed by irradiation of a solution of mercurous nitrate in diluted HNO_3.

Table of the results.

Volume in ml	Before irradiation			After irradiation			
	Dz.cpd. millimols	Hg_2^{++} millimols	HNO_3 N	Hg_2^{++} millimols	Hg^{++} millimols	Hg millimols	N_2-gas millimols
100	0.93	0.46	0.02	0.0	0.45	0.45	
150	1.34	1.34	0.04	0.0	1.42		1.37
150	1.34	1.34	0.04	0.0	1.38		1.35
150		0.67	0.02		0.0	0.0	

Eindhoven, April 1952.

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